

SOME NEW DOUBLE PHOSPHATES

By

LOUIS J. COHEN, M. S.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in the Faculty
of Pure Science of Columbia University

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INTRODUCTION.

In an unpublished paper J. L. Danziger states that by the addition of a large excess of diammonium phosphate to a solution of ferric chloride strongly acid with hydrochloric acid, he obtained a white powder which on analysis so closely approximated the formula $\text{NH}_4 \text{H}_2 \text{PO}_4 \cdot \text{FePO}_4$ as to warrant the belief in the existence of such a double phosphate of ferric iron. By the same method of precipitation, the existence of corresponding sodium and potassium salts was indicated although the latter products were not quantitatively analyzed.

The verification and extension of this preliminary work of Danziger, served as the object of this investigation.

L. J. C.

ACKNOWLEDGMENT.

This work was undertaken at the suggestion of the late Prof. E. H. Miller for whose advice and encouragement I take this opportunity of expressing my appreciation and indebtedness. I wish also to gratefully acknowledge my obligations to Prof. H. C. Sherman, Prof. J. L. R. Morgan and Dr. F. J. Metzger for valuable assistance.

L. J. C.

QUANTITATIVE LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
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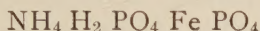
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EXPERIMENTAL.

THE DOUBLE PHOSPHATE OF IRON.



By closely following the method of Danziger, which consisted in adding an excess of diammonium phosphate to a strongly acid solution of ferric chloride, difficulty was at once met with in washing the precipitate formed, entirely free of phosphoric acid with cold water; for after hours of washing, the wash-water still gave a decided test for PO_4 . Further washing gave the same result. From the persistence of PO_4 in the wash-water in apparently uniform amounts, after considerable water had been employed, it became evident that the phosphoric acid in the wash-water was derived from some other source than either the excess of the reagent or by-products of the initial reaction. Accordingly a series of precipitates was prepared and washed with a limited though sufficient quantity of water. The products after drying at 100°C . were analyzed. Results low in phosphorus and ammonia were obtained. Repeated attempts to obtain a salt of normal composition by washing with water, the products formed under slightly varied conditions, gave substantially the same low figures for phosphorus and ammonia as shown below:

	Found.			Theory.
	A	B	C	
Fe	21.20%	21.10%	21.20%	21.05%
P	22.83%	22.40%	22.75%	23.30%
NH_4	6.31%	6.31%	5.96%	6.76%

These results are in agreement with those obtained by Danziger.

Fe	21.15%
P	22.95%

After considerable experimentation, the following method was found to yield a salt of normal composition.

A solution consisting of 200 cc of Ferric Chloride (containing 20 grams Fe Cl_3) 80 c.c. HCl (sp. gr. 1.2) and 120 c.c. water, was heated to about 70° . To this was added gradually and with constant stirring a hot solution of diammonium phosphate (120 grams in 200 cc of water). The color of the iron solution weakened with the addition of the phosphate and finally disappeared. Further addition of diammonium phosphate produced a creamy white flocculent precipitate which on prolonged heating on a boiling water bath, or with constant stirring on an asbestos pad heated by a Bunsen burner, was observed to change (at from 91° to 95°) to a perfectly white and powdery form resembling barium sulphate, leaving a clear colorless supernatant liquid. After digestion on a boiling water bath for one-half hour, the supernatant liquid was siphoned off and the residual compact mass washed several times by decantation with an alcoholic solution (1 part 95% alcohol to 2 parts water) containing 0.1 per cent. ammonium chloride, and finally washed on a filter with alcohol (1:1) till free of chlorides.¹ It was then dried at 100° in a water-oven and analyzed.

The iron was determined volumetrically with a standard potassium permanganate solution by the Zimmerman-Reinhart method; the phosphorus was separated from the iron in the usual way with ammonium molybdate solution, and ultimately weighed as magnesium pyrophosphate. The ammonia was determined by distillation with caustic potash into a standard acid solution.

	Found.	Theory for $\text{NH}_4 \text{H}_2 \text{PO}_4 \text{Fe PO}_4$
Fe	20.89%	21.01%
P	23.20%	23.30%
NH_4	6.60%	6.76%

Having obtained a salt of normal composition, it was thought desirable to ascertain the effect of water on this salt with a view to account for the low results obtained for phosphorus and ammonia in the first products which had been subjected to excessive washing with water. To this end 3 grams of the salt

¹ The final washings though free of chlorides gave a test for PO_4 with ammonium molybdate solution.

were treated in a flask with about a liter of water (at room temperature, 28°), the contents thoroughly agitated, allowed to settle and the clear liquid filtered. This was repeated until the combined washings measured six liters. The residual salt was dried at 100° and on comparison with the untreated sample appeared yellowish, thus indicating hydrolysis.

Analysis of the residue gave :

Fe	21.43%
P	22.40%
NH ₄	6.35%

Comparison of these figures with those obtained for the normal salt conclusively shows that the water dissolved out phosphorus and ammonia.*

An examination of the washings concentrated to 250 c. c. showed the absence of iron and the presence of ammonia and phosphorus; but the amounts of the latter were insufficient for an accurate quantitative estimation.

To intensify the hydrolytic effect of water 0.9921 gram of the normal salt was treated in a similar way as above with a liter of hot water 90° ; (the average temperature of the water at the time of filtration 66°) the operation was repeated with another liter of hot water. The residue was noticeably brownish-yellow after the first treatment. The filtrates were combined and evaporated in a platinum dish on a water-bath to dryness, then placed in a water-jacketed oven and finally weighed.

Weight of total residue was 0.1038 gram equal to 11.25 per cent. of the original salt. This residue was dissolved in water† made up of 250 c.c. and aliquot portions analyzed for phosphorus and ammonia.

Found :

P.	35.56%
NH ₄	14.94%

The amount of phosphorus in the filtrate is in excess over that necessary to form monammonium phosphate with the am-

* An explanation of this fact will be given at the end of this section.

† This solution was faintly acid to litmus and to congo red and gave no test for iron.

monia found. This excess as will be explained below is due to the hydrolysis of the ferric phosphate. The analysis of the residual salt after treatment with hot water gave:

Fe	21.95%
P	21.46%
NH ₄	5.61%

The deficiency in phosphorus and ammonia here indicated was found to be exactly compensated by the ammonia and phosphorus found in the wash-water.

The above experiments conclusively show that the action of water on the salt consists in dissolving out some phosphorus and ammonia accompanied by a change in color of the compound. The alcoholic solution (1:1) employed in the final washing of the salt also removed phosphorus, as shown by the presence of the latter in the washings after the complete removal of chlorides. Inasmuch as the amount of phosphoric acid found in the wash-water is in excess over that required to form monammonium phosphate* with the ammonia found, this excess must have been derived from the ferric phosphate. This conjecture is borne out by the investigations of Caven,¹ and verified by Cameron and Hurst,² which establish the hydrolysis of ferric phosphate by water beyond a doubt. That the darkening of the compound is also due to the hydrolysis of ferric phosphate is confirmed by the work of Caven¹, who treated his white variety of ferric phosphate with hot water and obtained a yellowish or brownish basic phosphate.

The presence of ammonia and the greater part of the phosphoric acid found in the water with which the normal salt was treated, may be accounted for by the slight solubility of the double salt with the subsequent dissociation into the soluble diammonium phosphate and the insoluble ferric phosphate; the latter yielding additional phosphoric acid by hydrolysis with

* As the solution was acid to congo red, no diammonium phosphate could have been present.

¹ Journ. Soc. Chem. Ind., 15, p. 17-19.

² Journ. Amer. Chem. Soc., 26, p. 885.

the simultaneous formation of an equivalent amount of ferric hydroxide.

The behavior of this double salt when subjected to excessive washing with water is not peculiar to this particular compound, but rather characteristic of a class of double alkali phosphates to which it belongs. A double phosphate of sodium and copper prepared by Steinschneider¹, and having the same type formula as the iron and ammonia salt, was observed when treated with water to undergo changes precisely similar to those already described for the double phosphate of iron and ammonium. In this case the loss of sodium and phosphoric acid was accompanied by a change in color from a beautiful blue to a greenish white. A corresponding double phosphate of ammonium and aluminum next to be described showed a similar behavior when treated with water.

Properties of $NH_4 H_2 PO_4 \cdot Fe PO_4$.

The double phosphate of ferric iron and ammonium readily dissolves in hydrochloric acid to a yellow solution; with nitric, sulphuric and phosphoric acids, colorless solutions are obtained. It is practically insoluble in 50 per cent. acetic acid. When treated with ammonia in the cold, partial hydrolysis takes place as indicated by the change in color from white to light brown; on prolonged heating, particularly when the ammonia is in great excess, the double phosphate completely dissolved to a reddish brown solution. Caustic alkalies completely hydrolyze the double salt. The solubility of the compound in phosphoric acid is noteworthy, because of its inability to reprecipitate on the addition of ammonia. If to a solution of the double salt in phosphoric acid, ammonia be added drop by drop, it acquires a yellow tint which deepens with the further addition of the reagent, but no precipitate was observed to form, even when sufficient ammonia had been added to render the solution strongly alkaline. A similar deportment was observed in a phosphoric acid solution of ferric phosphate prepared by adding dilute phosphoric acid to ferric chloride until the precipitate

¹ "Ueber die Phosphate des Kupfers"—Dr's. Dissertation Halle, a. S., 1890.

which first formed redissolved. From this solution, ammonia failed to precipitate either the hydroxide or phosphate of iron. These results find their explanation either in the solubility of the phosphate in ammonium phosphate, or as being due to the combination of ferric phosphate with phosphoric acid to form a complex phospho ferric acid. $H_3 Fe (PO_4)_2$ the iron of which is not precipitable by ammonia and of which the iron salt just described is a derivative. The latter supposition appears to be confirmed by the work of Erlenmeyer¹, who prepared a compound to which he assigned the formula $Fe_2 O_3 (P_2 O_5)_2 \cdot 8H_2O$, and which is resolved into $(H_2PO_4)_2 Fe_2 (HPO_4)_2$, and called the primary secondary ferri phosphate, and mono diferric phosphate. Arranged somewhat differently the structural formula becomes:



and simplified $H_2 PO_4 Fe H PO_4$ or $Fe H_3(PO_4)_2$. It is manifest that this is the hypothetical phosphoferric acid referred to above. When ignited, the double salt decomposes, giving off ammonia and water.

Further study of the action of ammonia:—

As the action of an excess of hot strong ammonia on the double salt seemed anomalous, further study was undertaken with a view to throw some light on the complex phosphate which doubtless formed, and which appeared to be soluble in an excess of ammonia. Freshly prepared ammonium ferric phosphate, after partially drying in the air, was treated in a beaker with a large excess of strong ammonia and heated on an asbestos pad. The white double salt first became brown, and on prolonged heating, finally dissolved with the formation of a deep reddish brown solution. A portion of this solution was poured into a crystallizing dish and allowed to evaporate spontaneously in the hope of crystallizing out a dissolved complex phosphate. On standing for several days, the concentrated solution was cleared up by the addition of more ammonia, and on further evaporation a syrup was obtained, which on prolonged exposure, was converted to a brown mass, but no crystals appeared.

¹ Studien über phosphosäure Salze, Lieb. Anhalen 194, p. 188.

Spontaneous evaporation of the ammoniacal solution having thus failed to yield a crystalline body, another portion was treated with 95 per cent. alcohol with the object of diminishing the solubility of any dissolved complex phosphate that the solution might hold. A brown voluminous gelatinous precipitate formed when an excess of 95 per cent. alcohol was added.

This was filtered and slightly washed with 95 per cent. alcohol and dried at 90°C. The filtrate possessed a slightly yellowish tint and gave a strong test for PO_4 .

Analysis of brown precipitate gave :

	A	B	Combining ratio.
Fe	32.64%	32.86%	0.581
P	14.94%	15.00%	0.482
NH_4	6.94%	6.96%	0.385

from which it appears that the ratio of iron to phosphorus to ammonia is 1.5 : 1.25 : 1 or 6 : 5 : 4 leading to the formula,



which is a basic double ammonium ferric phosphate. That this compound is basic might have been surmised from its color, and by the presence of phosphoric acid in the alcoholic filtrate. The assumption of the secondary ammonium phosphate instead of the tertiary in the formula seems justified because of the instability of the latter; for on drying, the tertiary salt would be hydrolyzed by the water or alcohol, to form the secondary phosphate, thus



The close agreement of the analytical results obtained, with those calculated for the formula above, confirms the above assumption.

	Found.	Calculated.
Fe	32.64%	32.37%
P	14.94%	14.93%
NH_4	6.94%	6.93%

THE DOUBLE PHOSPHATE OF ALUMINUM.



As no mention is made in the literature of a double phosphate of aluminum corresponding in composition to the double phosphate of iron just described, an attempt was made to prepare it. The method which yielded this salt was similar to that employed in the preparation of the iron salt, except as regards acidity, which in this case was somewhat greater.

Preparation—Ten grams of c.p. aluminum chloride were dissolved in 300 c.c. of hydrochloric acid (1-1) and the resulting solution heated to about 65° C. To this was added, with constant stirring, a hot saturated solution of diammonium phosphate and finally the solid salt till precipitation occurred. The volume at the time of precipitation was approximately 1000 c.c. and the amount of diammonium phosphate added 230 grams. The precipitate when first formed was gelatinous in character, resembling aluminum hydroxide; but on continued heating on an asbestos pad over a bunsen burner, and constantly stirring (to avoid bumping), the precipitate was observed to change at 90° to a dense powder, which rapidly settled on standing. The rise in temperature from 65° to 90° consumed one-half hour. The precipitate and clear solution were then heated on a boiling water-bath for one-half hour and then allowed to stand over night. The next day the clear solution was siphoned off and enough warm water added to dissolve the primary ammonium phosphate which crystallized over the white mass on the bottom of the beaker. The clear solution was again siphoned off and the residual white compact mass washed several times by decantation with an alcoholic solution (1:2) containing 0.1% $\text{NH}_4 \text{Cl}$ and finally transferred to a filter and washed with alcohol (1:1) till free of chlorides.*

It was then dried at 96°-98° in a water-jacketed oven and analyzed.

* The final washings though free of chloride gave a test for PO_4 .

The ammonia and phosphorus were determined by the same methods employed in the analysis of the iron salt. The aluminum was determined, with slight modification, by the method given by Crookes.* About one gram of the salt was dissolved in the least amount of concentrated hydrochloric acid, diluted somewhat, and an excess of a strong solution of sodium hydroxide (free of aluminum) added. The clear resulting solution was warmed and barium chloride added till no further precipitation occurred. The mixture was then digested at a gentle heat for one-half hour, filtered and the precipitated barium phosphate washed free of chlorides with a very dilute solution of sodium hydroxide. The filtrate after being slightly acidified with hydrochloric acid was concentrated to 250 c.c.; 100 c.c. of this solution were pipetted out, and after removing the barium with sulphuric acid, the aluminum was precipitated with ammonia and ignited to Al_2O_3 .

	Found.	Theory for $NH_4 H_2PO_4 \cdot Al PO_4$.
Al	11.53%	11.42%
P	26.16%	26.13%
NH_4	7.79%	7.61%

A salt prepared under slightly different conditions of acidity and concentration of the precipitant gave substantially the same results.

Al	11.29%
P.	25.77%
NH_4	7.63%

Properties of the Aluminum Salt—A qualitative study of the action of water on this salt, showed that it was hydrolyzed in precisely the same way as was noted in the case of the iron salt. Its solubilities are the same as those for the iron salt, except towards alkalis; in the latter it dissolves completely behaving like aluminum phosphate. On ignition it gives off ammonia and water.

* Crooke's Select Methods in Chemical Analysis, 4th Edit., p. 520.

THE CHROMIUM PHOSPHATES.

In attempting to prepare a double phosphate of chromium under the conditions of acidity already described in the formation of the iron and aluminum salts, negative results were obtained; no precipitate was formed even when an extremely large excess of diammonium phosphate was added. When, however, the acidity was diminished, a precipitate was readily obtained.

The chromium solution employed was prepared by treating a little more than twenty grams of Kahlbaum's chromium hydroxide with 45.2 c. c. of hydrochloric acid (1.2)*. After slightly warming, the volume was made up to 500 c. c., thoroughly mixed, allowed to stand and finally filtered from the undissolved hydroxide. The resulting clear solution was acid to litmus and contained approximately six grams of chromium chloride in 100 c. c.

As it was impossible to previously determine the acidity required to form a double phosphate, four precipitations were made yielding respectively the products "A," "B," "C," and "D," referred to below, from solutions containing varying amounts of hydrochloric acid; the total volume in each case being 400 c. c.

As the method of preparation was the same for all, a detailed description of one will suffice.

Sample A. A solution consisting of 100 c. c. of the chromium chloride solution, 90 c. c. of water and 10 c. c. of hydrochloric acid (1.2), was heated to 80°. To this was gradually added, with constant stirring, 50 grams of diammonium phosphate dissolved in 200 c.c. of water. The green precipitate which first formed was gelatinous in character, but on heating on an asbestos pad, for one-half hour, was observed to change at 90° to a dense and granular form, which rapidly settled, leaving a clear,

* This being the calculated amount of hydrochloric acid for the complete solution of 20 g. of the hydrate.

slightly green supernatant liquid. After digestion on a boiling water bath for one-half hour the clear liquid was siphoned off and the residual compact mass washed by decantation with alcohol (1:1), containing 0.1 per cent. ammonium chloride; and finally washed on a filter with alcohol (1:1) till free of chlorides; it was then dried in the water oven and analyzed. The supernatant liquid was acid to litmus, and gave a strong test for phosphoric acid and ammonia; showing that an excess of the precipitant had been added.

Sample B was prepared under the same conditions, except as regards acidity; which in this case was 15 c. c., in sample C, 1 c. c. was used; with sample D no acid was added.

The first filtrates from each of the last precipitates were slightly green, acid to litmus, and gave strong tests for phosphorus and ammonia, showing that an excess of the precipitant had been added.

There appeared to be scarcely any difference in the color of samples A, B and C, which were all light green.

Sample D possessed a bluish-slate color when first formed, which on continued heating acquired a violet tinge and finally on drying in the water oven became dark green.

Method of Analysis:—

In the analysis of the chromium compounds, considerable difficulty was encountered in the determination of phosphorus. The usual method of separation with ammonium molybdate in a nitric acid solution, was incomplete; the ammonium phosphomolybdate invariably carrying down with it appreciable amounts of chromium, as was shown by its olive color. Precipitating in a larger bulk, followed by thorough washing with dilute nitric acid solution having failed to remove the contamination, reprecipitation was resorted to. This gave a more yellow precipitate, but still retained chromium, as shown by the purple tint of its solution in ammonia, and by the slight color of the magnesium pyrophosphate obtained therefrom. Precipitation of the phosphorus with barium chloride in an alkaline solution, was next tried; but this method also failed to give a satisfactory separation. These methods were, therefore, abandoned, and

those based on the preliminary oxidation of the chromium tried; after some experimentation the following method was adopted.

About one gram of the sample was treated in a beaker with a solution of sodium hydroxide (prepared from Na) and warmed till complete solution took place. Sodium peroxide was then added in small amounts and the solution brought rapidly to a boil. After a clear yellow solution had been obtained, the boiling was continued for fifteen minutes, cooled, then neutralized with sulfuric acid, transferred to a 500 c.c. flask, and diluted to the mark. 50 c.c. were pipetted out, diluted to 150 c.c., and then made slightly alkaline with ammonia. The phosphorus was precipitated with magnesia mixture in the usual way and weighed as $Mg_2 P_2 O_7$. In the filtrate or in another 50 c.c., the chromium was determined volumetrically by titrating with standard hypo solution the iodine liberated.

The ammonia was determined in the usual way:

Found:

	Sample A.	Sample B.		Combining ratio calc. from B.
NH_4	7.71%	7.60%	7.55%	0.633
Cr	21.37%	21.30%	21.43%	0.411
P	18.61%	19.57%	19.63%	0.418

These figures show that the ratio of ammonia to chromium to phosphorus is 1.5: 1: 1 or 3: 2: 2, leading to the formula



Recalculating the analytical results on the dry basis we get

	Found.	Calculated.
$(N H_4)_2 O$	12.51%	12.47%
$Cr_2 O_3$	36.12%	36.45%
$P_2 O_5$	51.41%	51.07%

On the assumption that the compound contained three molecules of water at the temperature of drying we get

	Found	Theory for $(\text{NH}_4)_2 \text{HPO}_4 \cdot 2 \text{Cr PO}_4 \cdot 3 \text{H}_2\text{O}$
P	19.63%	19.36%
Cr	21.43%	21.69%
N H ₄	7.55%	7.52%

The close agreement sufficiently warrants the supposition that at the temperature of drying, the salt retains three molecules of water.

Analysis of samples C and D gave:

	C		D	Combining ratio calc. from D.
P	17.39%	17.36%	17.24%	0.556
Cr	23.83%	23.71%	24.43%	0.468
N H ₄	6.96%	6.74%	7.06%	0.392

The ratio of phosphorus to chromium to ammonia is 1.4:1.2:1 or 7:6:5 leading to the formula:



The results calculated for this formula agree with those found as shown below:

	Found D	Theory for $5 \text{NH}_4\text{H}_2\text{PO}_4 \cdot 2 \text{Cr PO}_4 \cdot 4 \text{Cr (OH)}_3$
P	17.24%	16.93%
Cr	24.43%	24.38%
N H ₄	7.06%	7.04%

The reduction of the acidity therefore results in the formation of a basic double phosphate. On ignition all the samples decompose giving off water and ammonia. The double chromium phosphates differ from those of aluminum and iron by their non-formation from strongly acid solutions, by their greater tendency to form basic salts and their ability to combine with the secondary ammonium phosphate.

THE DOUBLE PHOSPHATE OF CHROMIUM AND
SODIUM.

From the results of experiments with diammonium phosphate upon hydrochloric acid solutions of the chlorides of iron, aluminum and chromium, it seemed quite probable that corresponding sodium and potassium salts could be prepared by substituting the di-sodium and di-potassium phosphates respectively for the di-ammonium salt. In the case of the double chromium-phosphate, however, this supposition appeared to be contradicted by the work of the Bloxam¹, who, on boiling an acetic acid solution of a chromium salt with di-sodium phosphate, obtained a green precipitate which from the results of his analysis, he regards as a basic chromium phosphate retaining five molecules of water at 100°. He states that his product contained admixed impurities, but no mention is made of the nature and extent of the latter in the analytical results. The readiness with which these double phosphates hydrolyse when excessively washed with water (as pointed out on page 5), and it appears that Bloxam's product was so treated, and that no mention is made of the absence of sodium in his product, seem to show that he first obtained a double phosphate of sodium and chromium which on prolonged washing with water changed to the basic compound he finally obtained and analyzed. This supposition is strengthened by the work of Steinschneider², who found that on excessive washing, with water his double phosphate of sodium and copper was converted to a basic phosphate, which was free of sodium.

¹ Chem. News, 52 194-195.

² Über die phosphates des Kupfers, Dr's Dissertation, p. 35.

EXPERIMENTAL.

Preparation : To 40 cc. of the chromium chloride solution used in the previous preparations, diluted to 100 cc., sodium hydroxide was added until a slight but permanent precipitate formed ; after clearing with a drop or two of acetic acid, 20 cc. more of 50 per cent. acetic acid was added and the resulting solution heated on an asbestos pad ; 50 grams of disodium phosphate dissolved in 200 cc. of water were then gradually added with constant stirring and the volume made up to 400 cc. The resulting clear solution was then heated ; no precipitate formed at first, but on continued heating a cloudiness soon formed followed by the formation of a green gelatinous precipitate which on further heating to 100° became dense ; it was then transferred to a boiling water bath for a half hour and allowed to stand over night. The next day the clear, colorless, supernatant liquid was siphoned off ; it was found to be acid and gave a strong test for PO_4 . The precipitate was washed twice by decantation with alcohol (1:1) then transferred to a filter and washed again with alcohol (1:1) till free of chloride ; it was then dried in a water oven and analyzed.

The dried precipitate possessed a green color, considerably lighter than that of any of the chromium compounds already mentioned.

Analysis gave :

		Combining ratio.
Cr	19.45%	.372
P	17.56%	.566
Na	8.79%	.382

showing that the ratio of chromium to phosphorus to sodium is 1 : 1.5 : 1, or 2 : 3 : 2, pointing to the formula $\text{Na}_2\text{HPO}_4 \cdot 2\text{CrPO}_4$.

Calculating our results on the dry basis we get :

	Found.	Calculated.
Cr_2O_3	35.30%	35.59%
P_2O_5	49.96%	49.87%
Na_2O	14.72%	14.52%

On the supposition that the salt contained 5 molecules of water at the temperature of drying we get:

	Found.	Calculated for $\text{Na}_2 \text{HPO}_4 \cdot 2 \text{Cr PO}_4 \cdot 5 \text{H}_2\text{O}$.
Cr	19.45%	19.77%
P	17.56%	17.68%
Na	8.79%	8.75%

These results fully confirm the supposition to which the results of Bloxam's basic chromium phosphate led, viz., that the addition of disodium phosphate to a solution of chromium chloride precipitates a double phosphate of chromium and sodium which readily hydrolyses on excessive washing with water to a basic phosphate.

CONCLUSIONS.

1. The addition of a slight excess of diammonium phosphate to a hydrochloric acid solution of ferric chloride precipitates a double phosphate of iron of the formula



which is perfectly white, soluble in mineral acids and readily hydrolyzed by water and ammonia; prolonged boiling with hot ammonia dissolves the salt with the formation of a reddish brown solution from which 95 per cent. alcohol precipitates a basic double phosphate. On ignition, the double salt decomposes, giving off ammonia and water.

2. When aluminum chloride is used instead of iron, a corresponding double phosphate forms of the formula



having the same solubilities as the iron salt, except towards alkalis; in the latter it dissolves completely, behaving like aluminum phosphate. On ignition, it gives off ammonia and water.

3. With solutions of chromium chloride under the condition of acidity mentioned, diammonium phosphate precipitates a double salt of the formula $(\text{NH}_4)_2 \text{H PO}_4 \cdot 2 \text{Cr PO}_4$ possessing a green color and retaining three molecules of water at 98°C . When the acidity is reduced, a basic double phosphate forms.

4. The addition of di-sodium phosphate to an acetic acid solution of chromium chloride, precipitates a double phosphate of the formula $\text{Na}_2 \text{H PO}_4 \cdot 2 \text{Cr PO}_4$, which retains five molecules of water at 98° , and which is considerably lighter in color than the corresponding ammonium salt.

5. All the compounds above enumerated readily hydrolyze with water.

BIOGRAPHICAL.

Louis J. Cohen entered the College of the City of New York in September, 1894, and was graduated in June, 1899, receiving the degree of B. S.

From 1901 to 1902 pursued graduate work in chemistry at New York University and received the degree of M. S. in 1902. In October, 1903, entered Columbia University and studied under Faculty of Pure Science for the degree of Ph.D. until June, 1907.

